Redox Potentials and Electronic States of Iron Porphyrin IX Adsorbed on Single Crystal Gold Electrode Surfaces

Metalloporphyrins are active sites in metalloproteins and synthetic catalysts. They have also been studied extensively by electrochemistry as well as being prominent targets in electrochemical scanning tunneling microscopy (STM). Previous studies of FePPIX adsorbed on graphite and alkylthiol modified Au electrodes showed a pair of reversible Fe(III/II)PPIX peaks at about -0.41 V (vs NHE) at high solution pH. We recently used iron protoporphyrin IX (FePPIX) as an intercalating probe for long-range electrochemical electron transfer through a G-quadruplex oligonucleotide (DNAzyme); this study disclosed two, rather than a single pair of voltammetric peaks with a new and dominating peak, shifted 200 mV positive relative to the approximate to-0.4 V peak. Prompted by this unexpected observation, we report here a study of the voltammetry of FePPIX itself on single-crystal Au(111), (100), and (110) and polycrystalline Au electrode surfaces. In all cases the dominating pair of new Fe(III/II)PPIX redox peaks, shifted positively by more than 200 mV compared to those of previous studies appeared. This observation is supported by density functional theory (DFT) which shows that strong dispersion forces in the FePPIX/Au electronic interaction drive the midpoint potential toward positive values. The FePPIX spin states depend on interaction with the Au(111) interface, converting all the Fe(II)/(III)PPIX species into low-spin states. These results support electrochemical evidence for the nature of the electronic coupling between FePPIX and Au-surfaces, and the electronic states of adsorbate molecules, with a bearing also on recent reports of magnetic FePPIX/Au(111) interactions in ultrahigh vacuum (UHV).